SELECTIVE R.T.L.P.C.V.D. OF TUNGSTEN BY SILANE REDUCTION ON PATTERNED PPQ/Si WAFERS

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ABSTRACT : Organic dielectrics are an attractive alternative to silicon oxide commonly used in multilevel metallization schemes. In this work, tungsten films are selectively deposited on substrates covered by patterned organic dielectric through a Rapid Thermal Low Pressure Chemical Vapor Deposition system by using the $\text{WF}_6\text{-SiH}_4\text{-H}_2$ gas phase. In the entire range of parameters, $\alpha\text{-W}$ is the only phase obtained. The resistivity of the films is about $20\ \mu\Omega\cdot\text{cm}$. The SiH_4/WF_6 ratio and the deposition temperature appear to be the decisive parameters. With determined optimal experimental conditions (SiH_4/WF_6 ratio of $3/4$ and deposition temperature of 350°C) W films are deposited with a good selectivity at $400\ \text{nm}/\text{min}$. These characteristics are improved when the etched area/wafer area ratio (called "load ratio") decreases. Adherence problems limit the thickness of the deposited W films. The maximum thickness is higher when deposition occurs on chromium covered silicon rather than on bare silicon.

I. INTRODUCTION

V.L.S.I. packaging technology for high performance systems in electronics have created a demand for high density multilayer interconnections. The tungsten Chemical Vapor Deposition (C.V.D.) is a good candidate for via filling because of its useful materials properties (for example its low specific contact resistance) . Its main advantage is that it can be selectively deposited on bare silicon but not on silicon dioxide.

Because of their low permittivity value ($\epsilon < 3.5$), polymer dielectrics are now preferred to the conventional silicon oxide ($\epsilon = 4$) or to the silicon nitride ($\epsilon = 7$). Among them, polyphenylquinoxaline (PPQ) has a high thermal stability, a low moisture adsorption ($< 1\%$) and a permittivity value as low as 2.8 (1).

To achieve selective W deposition on silicon substrate covered with patterned PPQ, the chosen way is the reduction of the WF_6 molecule. The reducing agent can be the silicon of the substrate. But in this case, the process involves a silicon consumption and the W growth is limited by the diffusion of the silicon into the deposited film. The use of H_2 as a reducing agent allows thicker films to be deposited. Moreover, for a reasonable throughput, the growth rate has to be high since via contacts are usually a few microns deep. The $\text{WF}_6\text{-H}_2$ chemistry cannot achieve such a growth rate even at high temperature (exceeding 500°C) and in any

case, organic dielectrics cannot withstand temperature greater than 400°C. Recently, it was reported that silane (SiH_4) is also an effective reducing agent providing very high growth rates of selective deposition even at low temperature (2).

Several studies show that the use of infra-red lamps instead of resistive ovens guarantee very high deposition rates (3). In conjunction with a small cold wall reactor, such a system (called Rapid Thermal Low Pressure Chemical Vapor Deposition) ensures a low contamination level required for the selective processes.

In this paper, we report the selective deposition of W on silicon substrate covered with patterned PPQ through a R.T.L.P.C.V.D. system with the $\text{WF}_6\text{-SiH}_4\text{-H}_2$ starting gaseous phase.

II. EXPERIMENTAL

A) Deposition system:

A scheme of the R.T.L.P.C.V.D. reactor used is shown on fig. 1. It is a commercial R & D FAV4 JIPELEC machine. All its walls are water cooled and the 100 mm diameter wafer is heated by a tungsten infra-red lamps arrangement through two quartz windows separated by a cooling water flow.

fig. 1 : scheme of the R.T.L.P.C.V.D. reactor

The standard pyrometers (wave length of 5 μm) are not fitted for use at our low temperatures (ranged from 250 to 400°C) and the heating at constant electrical power is not satisfactory. Indeed, as the W film grows, the reflectivity of the substrate upper face changes which involves great temperature variations. So the FAV4 system is equipped with an IRCON MODLINE pyrometer (wave length of 8 to 10 μm) allowing temperature measurements as low

as 100°C. The substrate temperature response is very high so it is used to switch the deposition process on and off. Unreacted and by-product gases are evacuated by a 350 m³/h roots pump which is backed by a 60 m³/h mechanical pump.

B) Substrates:

Substrates are (100) oriented silicon wafers of 4 inches diameter covered by a SiO₂/Si₃N₄ bilayer of 25/90 nm thick. The PPQ, prepared in solution in a O-xylene, m-Cresol is spun on it at the desired thickness by adjusting the rotation speed and the PPQ concentration. Typically, 2.5 µm thick films are obtained at 3500 rpm for PPQ concentration of 12% in weight. After deposition, complete solvent evaporation is achieved in a low temperature annealing step. Further polymer densification is performed by heating it at 400°C (its glass transition temperature is 350°C) and the thermal cure process occurs in a tubular oven under a nitrogen flux (1).

Then the PPQ layer is patterned according to give holes and lines of 10 mm to 12 µm wide.

III. RESULTS AND DISCUSSION

As the use of R.T.L.P.C.V.D. system leads to very high deposition rates (for example for silicon or titanium silicide deposition (3)), the first step of this study is to evaluate the W deposition from WF₆-H₂ gas mixture. The results concerning the selectivity, the resistivity (7 to 10 µΩ.cm) and the adherence are quite similar to those obtained in a standard hot wall L.P.C.V.D. system (4) except the growth rate is ten times higher (100 nm/min at 400°C).

However, much higher growth rates are required for via filling applications and cannot be reached in the PPQ stability temperature range. So this study is carried out by using the SiH₄-WF₆-H₂ gas mixture on different types of wafers.

A) PPQ/Si substrates

Among all the experimental parameters, the SiH₄/WF₆ ratio and the deposition temperature appear to be decisive for the selectivity and the resistivity of the deposited layer. So the H₂ and WF₆ flow rates are fixed at 150 and 10 sccm/min respectively and the SiH₄ flow rate varies from 3 to 15 sccm/min, while the deposition temperature ranges from 250 to 400°C. The total pressure is about 30 Pa.

First, it must be noticed that whatever the SiH₄/WF₆ ratio and the deposition temperature may be, only α-W phase is observed in the film by X-ray diffraction.

1. SiH₄/WF₆ ratio influence

The silane addition increases significantly the W growth rate only for a SiH₄/WF₆ ratio higher than 3/4. For example, at 350°C, with a 3 sccm/min SiH₄ flow rate, the growth rate is 150 nm/min and for a 7.5 sccm/min SiH₄ flow rate, the growth rate reaches 400 nm/min.

For higher SiH₄/WF₆ ratio, the growth rate still increases to 1 µm/min but the selectivity is impaired and gets increasingly (fig. 2).

fig. 2 : Dark field optical micrographs showing a selectivity of:

- a) 250 pts/mm² for a SiH₄/WF₆ ratio of 3/4
- b) 830 pts/mm² for a SiH₄/WF₆ ratio of 1

fig. 3 : RBS spectra of W films deposited with :

- a) a SiH_4/WF_6 ratio of 1
- b) a SiH_4/WF_6 ratio of 3/4

Moreover, RBS spectra (fig. 3) show silicon incorporations in the whole film involving high resistivity. Hence, at 350°C, when the SiH₄/WF₆ ratio varies from 3/4 to 1, the resistivity increases from 20 μΩ.cm to 150 μΩ.cm.

2. Deposition temperature influence

The influence of the deposition temperature is studied for a SiH₄/WF₆ ratio of 3/4. Within the narrow deposition temperature range, the growth rate remains nearly constant (5) but the selectivity is strongly affected.

In order to evaluate the selectivity evolution, the number of the W nuclei on the PPQ surface is counted within a 0.01 mm² area using a dark field optical microscope at a magnification of 200 for different temperature values (fig.4). As it can be seen, the nuclei density falls rapidly for a temperature increase until 250 pts/mm² at 350°C and then slightly increases again (1600 pts/mm² at 375°C).

fig. 4 : Number of W nuclei per mm² on the PPQ versus temperature for a SiH₄/WF₆ ratio of 3/4

The resistivity does not seem to be affected by the deposition temperature which means that silicon content is only due to a silane excess in the gas mixture.

However, we can observe that high deposition temperatures lead to adherent films (according to the scotch tape test) up to thicknesses of 0.8 μm, while low deposition temperatures allow the film to be adherent only for thin films (for example, W deposit peels off for thicknesses higher than 0.2 μm at 250°C).

B) PPQ/Cr substrates

In order to improve the adherence, the hole bottom is covered with a chromium layer on which the W film grows. The influence of both parameters: SiH_4/WF_6 ratio and deposition temperature on the growth rate, the selectivity and the silicon content (therefore the resistivity) is quite similar.

However, adherent films can now be deposited up to about 1 μm in thickness. But, for higher thicknesses, W deposit still peels off from the Cr surface.

C) Load ratio influence

The etched area/wafer area ratio (which may be called "load ratio") could play a significant part in the selectivity. Hence, for a low load ratio, the selectivity is absolute (no W nuclei can be observed with dark field optical microscope). As the load ratio is increasing, more and more W nuclei appear especially in the vicinity of large area W plots. This result is explained by the reaction between WF_6 and deposited W leading to a W transport from the W surface to adjacent PPQ covered surface (6).

Moreover, high load ratios involve a great reactive gas consumption leading to a growth rate decrease. Hence, the growth rate of about 400 nm/min for a load ratio of 25% is reduced by half for a 100% one.

CONCLUSION

Selective W deposition on patterned PPQ wafers was achieved with a R.T.L.P.C.V.D. system. The use of WF_6/H_2 gas mixture requires too high deposition temperatures with respect to the PPQ thermal stability and leads to growth rates too low for via filling application.

In contrast, the WF_6 reduction by silane provides higher growth rates even at low temperature and α -W phase is always observed in the deposited film.

The influences of the SiH_4/WF_6 ratio, of the deposition temperature and of the load ratio are investigated. Optimal experimental parameters to obtain a good selectivity (200 pts/ mm^2) as well as low resistivity (20 $\mu\Omega\cdot\text{cm}$) with high growth rates (400 nm/min) are determined (SiH_4/WF_6 ratio of 3/4, deposition temperature of 350°C and reduced load ratio)

Because of some adherence failure, the thickness is limited to 0.8 μm on silicon wafers. By depositing on chromium covered silicon wafers, the deposited W thickness can be increased to 1 μm .

The adherence problems are still not well understood, therefore we will carry on this study by attempting to use different bonding layers.

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